Distribution of Chromium Species and Physico-Chemical Analysis of Various Industrial Effluents in Hyderabad and Jamshoro, Pakistan

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Abstract: This research aimed to quantify the speciation of chromium in different industrial effluent samples of Hyderabad and Jamshoro, Pakistan. The hexavalent chromium (Cr(VI)) was determined by microsample injection system flame atomic absorption spectroscopy (MIS-FAAS). The total chromium was measured by MIS-FAAS after the oxidation of trivalent chromium (Cr(III)) to hexavalent chromium (Cr(VI)) by $Ce(SO_4)_2$ in an acidic medium (0.07 M H_2SO_4). The content of Cr(III) was measured by the difference method (total chromium – hexavalent chromium). In the effluent samples of textile and fabrics industries, the total Cr was observed 400 to 1600 times higher than the US-EPA and WHO regulatory limit (0.10 mg/L) in the industrial discharge. In the effluent of food and plastic industries, the Cr(VI) was found to be high as compared to the Cr(III), and the Cr(III) was observed high in the effluent samples of chemical as well as textile and fabrics industries. The Cr(VI) was higher than the US-EPA and WHO regulatory limit (0.05 mg/L) in the effluent samples of all selected industries, but the Cr(III) was within the US-EPA and WHO regulatory limit (170 mg/L) in the industrial discharges.

Keywords: Chromium; Solid phase extraction; Micro sample injection system; Flame atomic absorption; Industrial effluent.

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1. INTRODUCTION

Industrial effluent is one of the main direct and often continuous input sources of pollutants into aquatic systems. These pollutants have long-term impacts on natural ecosystems, including changes in food availability and a grave threat to the ability of the biosphere to self-regulate . The industrial discharges or wastes have heavy metals, polychlorinated biphenyls (PCBs), pesticides, dioxins, polycyclic hydrocarbons (PAHs), phenolic compounds, and petrochemicals and microorganisms. All the industrial effluents are usually discharged into the natural water resources such as rivers and lakes, and cumulative hazardous consequences on the ecosystem have received a lot of attention. Untreated municipal and industrial wastewater has posed serious environmental risks to humanity. Industrial effluent discharge is a potential source of environmental pollution throughout the world . In Pakistan, the untreated effluents are either released to the agricultural land for irrigation purposes or disposed of in the nearby water bodies due to a lack of sewage treatment plants. Thus, the contaminants are either accumulated in soil or may enter through the food chain to generate several occupational health consequences . The pollution of heavy metals from industrial effluent has become a major public and scientific problem because of their hazardous effects on humans and other biological pathways. The increasing influx of heavy metals can be dispersed by water and wind, which make them accessible to animals and plants . Therefore, the information on toxic metals, especially chromium (Cr), and its different forms found in industrial effluents. It is important because of their relative toxicity, which may depend on their chemical properties and bioavailability.

The significance of chromium (Cr) speciation is associated with its toxic effects on different oxidation states. The Cr(III) and Cr(VI) are two stable chromium species found in the environment. Cr(III) is a relatively non-toxic and essential nutrient for humans, especially mammals, for their appropriate carbohydrate tolerance factor, protein, and lipid metabolism . The toxic effects of Cr(VI) are common due to its higher oxidation state and relatively smaller in size, allowing it to pass through the cell membranes and cause serious damage to proteins, DNA, and other macromolecules. The Cr(VI) suppresses the cell's enzymatic sulfur uptake and affects the lungs, kidneys, and liver. The major toxic effects of Cr(VI) include dermatitis, chronic ulcers, the corrosive reaction of the nasal septum, and lung infections . However, the determination of chromium is crucial with appropriate accuracy and sensitivity. The Cr species are usually discharged into the natural water resources due to different industrial activities, such as leather tanning, electroplating, steel works, pigments, refractories, oxidative dyeing, and lumber processing. In the water bodies, the Cr species usually exist in the form of chromate and hydroxo-complexes . Several strategies like coprecipitation, solvent extraction, electrochemical methods, solid phase extraction (SPE), ion-exchange separation, capillary electrophoresis, and ion chromatography have been developed for the determination of Cr species in different oxidation states (Cr(III), and Cr(VI) . SPE has some advantages over the techniques mentioned earlier in the speciation analysis of Cr because of its safety, flexibility, environment-friendly, selectivity, absence of emulsion, ease of automation, and simplicity. Amberlite XAD resins have been extensively used in SPE for various metals because of their cross-linked polymeric nature, which enhances their adsorptive properties due to their macro reticular type structure and greater active surface area . This macro reticular structure exhibits excellent chemical, mechanical, and thermal stability, making it an excellent candidate for the adsorption of various metal ions. In the ground waterway, Cr pollution has been reported as a result of the environmental effects of industrial wastewater drainage by the tanning industry . It may alter the pH, and enhances the biochemical oxygen demand (BOD), total dissolved solids (TDS), and electric conductivity (EC), which may give intense colourations to rivers . Therefore, the ecology is highly affected by microbial populations, which could be poisonous, mutagenic, or carcinogenic for aquatic animals . Based on these facts, the gradual monitoring and assessment of Cr and its different forms in industrial effluents are very important. Moreover, the effect of different quality parameters of industrial effluents on the mobility of Cr species is the need of hours.

The total Cr and its species in Hyderabad and Jamshoro district industrial effluents were investigated. The Cr(VI) was determined by a solid phase extraction procedure using Amberlite XAD-4 resin . At the same time, Cr(III) was calculated by subtracting Cr(VI) concentration from total Cr in the studied industrial effluent samples. The variation of physical quality parameters like pH, BOD, TDS, and EC in different industries has been quantified.

2. MATERIAL AND METHOD

2.1. Reagents and Glassware

The analytical grade nitric acid ($HNO_3 \geq 65$ % with Sp.gr: 1.41) and hydrogen peroxide ($H_2O_2 \geq 30$ % with Sp.gr: 1.11) were purchased from Merck (Germany). A certified standard solution of Cr (1000 mg/L, Fluka Kamica, Switzerland) was used to calibrate the quantitative determination of total Cr. For Cr(VI), the calibration curve was drawn using a standard solution of $K_2Cr_2O_7$ (dissolving 0.372 g of $K_2Cr_2O_7$ in 1.0 L deionized water), and 1.0 M HNO_3 was used to prepare appropriate dilute solutions. Deionized water (electrical conductivity 0.050 µs/cm) was prepared by the water purification system of ELGA laboratory (Bucks, UK). The adsorbent, Amberlite XAD-4, with surface area and pore diameter of 735 m^2/g and 20–50 µm, respectively, were used. Before use, all glassware (pyrex) and plastic (polyethylene) bottles were carefully washed. The glasswares were soaked in 5.0 M HNO_3 for 24 hours, then rinsed with deionized water.

2.2. Instrumentation

The concentration of Cr was determined using a flame atomic absorption spectrometer (Hitachi model 180-50; Tokyo, Japan) equipped with Cr hollow cathode lamp (HCL), and a flame atomizer (air-acetylene). The wavelength, spectral bandwidths, and lamp current were used as 358.0 nm, 0.70 nm, and 25.0 mA, respectively.

2.3. Preparation of Column

The preconcentration of Cr was achieved using a 15.0 cm long, 1.2 cm diameter glass column. The column was packed up to the height of 4.0 cm with a slurry of 1.2 g Amberlite XAD-4 resin in 25.0 mL deionized water. The adsorbent material was properly settled by using glass wool at the top and bottom of the column then 0.1 M H_2SO_4 was used to activate the column.

2.4. Sample Collection

Random samples of industrial effluents were collected from twenty industrial effluents of Hyderabad and Jamshoro, Pakistan, located at different places. These industries were divided into four categories based on their natural food industry (FI), plastic industry (PI), chemical industry (CI), and textile and fabrics industry (TFI). For sampling, ten samples were randomly collected from two to three industries for each category of industry (n = 40). Microbiological examination vials of 500.0 mL capacity were used to collect the industrial effluent samples, and the physicochemical parameters such as biological oxygen demand (BOD), total dissolved solids (TDS), pH, and electric conductivity (EC) of each sample were analyzed by the method described by AOAC .

2.5. Determination of Hexavalent Chromium

The Cr(VI) content was determined by solid phase extraction (SPE), as reported by Rajesh et al. 2008 . For SPE, a 1.0 mL of 10.0 mg/L solution of Cr(VI) was added to a 100 mL volumetric flask along with 3.0 mL of 0.5 M H_2SO_4, followed by the addition of 3.0 mL of 0.25 % diphenylcarbazide and the solution mixture was diluted up to the mark with deionized water. The sample solution was loaded onto the column containing Amberlite XAD-4 resin, maintaining a flow rate of 2.0 mL/min. The Cr-diphenylcarbazide complex (reddish violet colored) was adsorbed onto the column, which was evident from the absorbance of the resulting solution. The adsorbed complex was then eluted using 15.0 mL of 2.5 M H_2SO_4 in acetone. The solution was placed on the hot plate to evaporate the acetone and added 5.0 mL of 0.2 N HNO_3 solutions in the residue. The solution was filtered with filter paper, and the concentration of Cr(VI) was determined by micro-sample injection system flame atomic absorption spectrophotometry (MIS-FAAS) as reported by Baig et al. 2012 .

2.6. Determination of Total Chromium

The total Cr was also determined by SPE MIS-FAAS after the oxidation of Cr(III) to Cr(VI) by using $Ce(SO_4)_2$, as reported by Baig et al. 2012 . The Ce(IV) in acidic media (0.07 mol/L, H_2SO_4) is used to oxidize Cr(III) to Cr(VI), and the resulted solution was treated as mentioned in the section on the determination of Cr(VI).

2.7. Calculation of Trivalent Chromium

The contents of Cr(III) could not be determined directly by the above analytical procedure, but their concentrations were given by the difference between the total Cr and Cr(VI) .

2.8. Analytical Figure of Merits

The analytical characteristics of the developed approach for determining Cr were calculated using optimized instrumental conditions. The standard addition method was used to draw the calibration curve for the determination Cr(VI) by SPE MIS–FAAS . The limit of detection and quantification (LOD and LOQ) of the developed method were calculated as 3×S/*m* and 10×S/*m*, respectively. Where S is the standard deviation (std.) of blank signals (n = 10) and *m* is the slope of the linear calibration graph . The LOD and LOQ of the developed approach for determining Cr(VI) were found to be 0.037 and 0.124 mg/L, respectively. The calibration curve of Cr(VI) for this interval was determined by the regression equation $A = 1.47\times10^{-2}$ [Cr(VI)] + 3.00×10^{-5}. Where, A is the analytical signal (absorbance in nm) and [Cr(VI)] is the concentration of analyte (Cr(VI)) in the sample solution (mg/L). The calculated coefficient of determination (R^2) for Cr(VI) was about 0.996.

The precision of the developed analytical approach was evaluated by percent relative standard deviation (%RSD) for each analyzed concentration, and %RSD was calculated as (Std./X)100, where Std stands for a standard deviation for seven measurements and X is the mean value of these measurements. The %RSD of method was found to be < 1.50 % (n = 6). The reliability of the developed method for determining Cr(VI) by SPE MIS-FAAS in the aqueous medium was evaluated by spiking the three known concentrations of Cr(VI) in the concentration range of 10.0 – 30.0 mg/L, and percentage recoveries were found to be> 99.0 % (Table 1).

Table 1: The results for the test of standard addition/recovery for Cr(VI) by solid phase extraction in industrial effluent samples (n = 6).

	Amount added (mg/L)	Found values Mean ± Std. (mg/L)	%Recovery [a]	%RSD
Cr(VI)	---	14.72 ± 0.18	--	0.37
	10.00	24.64 ± 0.13	99.20	1.09
	20.00	34.82 ± 0.23	100.5	0.75
	30.00	45.32 ± 0.11	102.0	0.91

[a] $$\%\text{Recovery} = \frac{C_{\text{after spiked}} - C_{\text{initial}}}{C_{\text{spiked}}} \times 100$$

2.9. Statistical Evaluation

Excel 2003 (Microsoft Office ®) and STATISTICA 6 (StatSoft, Inc.®) were used to perform all mathematical and statistical calculations. Means ± SD, and Student's t-test were used to express the distributed data to evaluate linear associations between physical quality measures and total Cr, and Pearson correlation coefficients were determined. All of the tests were two-sided with a 0.05 p-value significant.

3. RESULT AND DISCUSSION

In all the analyzed effluent samples, the temperature had a distinct annual cycle, in which the summer season showed higher values and the winter season showed lower values. The results of physicochemical parameters (pH, EC, TDS, and BOD) of industrial effluent samples (collected from four different industries) are shown in Table 2. The pH values of effluent samples of FI, PI, CI, and TFI were 7.00 – 8.60, 6.60 – 6.80, 6.70 – 7.90, and 6.10 – 6.6 respectively (Table 2). PI and TFI are slightly acidic because of various chemicals in these sectors' cleaning, washing, and polymerization/dying processes . The effluents had a slightly acidic pH (5.96 ± 0.09) and the exposure pH should be higher (7.16 ± 0.02). The basic pH of the natural water may cause damage to the fish's outer surfaces, such as the skin, eyes, and gills, and render them unable to dispose of metabolic wastes .

However, the highly acidic industrial effluents may enhance the toxicity of the organic compounds . The TDS were found at 951-1820, 1348-1382, 1348-1382, and 450-1322 mg/L in FI, PI, CI, and TFI industrial effluents samples.

The EC of industrial effluents (FI, PI, CI, and TFI) were found in the range of 0.87-4.01, 3.00-3.60, 2.88-3.72, 0.40-5.30 mS/cm, respectively. The EC of all the analyzed industrial effluents was greater than US-EPA allowed limits (1.00 mS/cm) for industrial effluents. The higher concentration of EC may be due to the dissociation of the dissolved substances present in the samples, concentration of ions, degree of dissociation, and temperature. The EC values of the effluent samples collected from FI were found to be higher than the other three industrial effluents ($p < 0.05$). The highest values of EC were found in TFI effluent samples. These may result from the released oil, grease, ammonia, sulfide, and dyes alongside the wastage effluents of TFI, which may also contaminate drinking water . These industries may be released a large quantity of residual chemicals and biological material waste into natural water sources such as rivers and canals without proper treatment, which may cause several health issues. The level of BOD was found at 475 ± 61.4, 575 ± 7.10, 565 ± 7.10, and 580 ± 20.0 mg/L in the analyzed effluent samples of FI, PI, CI and TFI, respectively as shown in Table 2.

Table 2: Physico-chemical characteristics of industrial effluents of Hyderabad and Jamshoro-Pakistan.

		pH	**TDS (mg/L)**	**EC (mS/cm)**	**BOD (mg/L)**
FI (n = 30)	Mean ± Std.	7.60±0.80	1403±435.00	2.33±1.57	47.5±6.10
	Range	7.00-8.60	951-1820	0.87-4.01	40.5-52.0
PI (n = 30)	Mean ± Std.	6.70±0.10	1365±20.01	3.30±0.30	57.5±5.10
	Range	6.60-6.80	1348-1382	3.00-3.60	57.0-58.0
CI (n = 30)	Mean ± Std.	7.20±0.50	1365±24.04	3.30±0.42	56.5±7.06
	Range	6.70-7.70	1348-1382	2.88-3.72	55.8-57.5
TFI (n = 30)	Mean ± Std.	6.30±0.20	951±491.01	2.83±2.45	58.0±2.00
	Range	6.10-6.60	450-1322	0.40-5.30	56.0-60.0

Std. = Standard Deviation

The BOD levels in all the analyzed effluent samples were observed at 8.0 to 12.0 times higher than the US EPA's recommended tolerance limit (50 mg/L) for industrial effluent discharge into rivers. The high level of BOD in effluent samples of all the industrial sectors might be attributed to the elevated concentration of organic matter produced by several chemicals utilized in the various industrial processes. However, a high level of BOD was observed in TFI effluent samples compared to other industrial effluents. It might be due to different chemicals used in textile industries for mercerizing, bleaching/scouring, and yawing, which include sodium chloride, sodium sulfite, NaCl, sodium bisulfate, sodium bicarbonate, formic acid, H_2SO_4, vegetable tannins, resins, sodium formate, polyurethane, fat emulsions, dyes, binders, waxes, pigments, lacquers/formaldehyde, NaOH, sodium phosphate, sodium hypochlorite, acids, H_2O_2, surfactants, Cl_2, and $NaSiO_3$. The findings of the current work showed that the difference among industries was statistically significantly different from each other ($P< 0.05$). Moreover, it was observed that the effluents from the studied industries remained continuously discharged into the nearby natural waterbodies during the sampling period.

The total Cr contents in effluents of FI, PI, CI and TFI varied between 30.0-38.0, 23.0-27.0, 35.0-95.0, and 40.0-180 mg/L respectively (Table 3). However, the total Cr concentration in the selected four industries increased as PI < FI < CI < TFI, with TFI showing the highest Cr concentration. The total Cr levels in the effluent samples analyzed from all the industrial sectors were higher than the US EPA standard for total Cr (0.10 mg/L) . The possible sources of Cr in these industrial effluents are the Cr compounds employed for various industrial applications like catalysts, dyers, and modifiers among others. The total Cr contents showed significantly positive correlation with pH, TDS and EC in effluent samples of FI ($r > 0.60$; $p < 0.001$), while strongly negative correlation was observed between total Cr and BOD ($r= -0.821$; $p < 0.001$). The total Cr contents in effluent samples of PI were reversely correlated with pH and TDS ($r > -0.90$; $p < 0.0001$), whereas, it has significantly correlation with EC and BOD ($r > 0.80$; $p < 0.0001$). On the other hand, the total Cr contents of effluent samples of CI have no significant correlation with the four studied physical parameters($P > 0.140$). It might be due to the low variation in the contents of total Cr in different effluent samples of CI of the Jamshoro district. However, total Cr levels have positive correlation with pH and TDS ($r > 0.60$; $p < 0.001$) and negative correlation with EC and BOD ($r > -0.60$; $p < 0.001$) (Table 4).

The Chromium speciation in industrial effluent is very important in determining the level of contamination and toxicity. Chromium speciation in industrial effluent samples of FI, PI, CI and TFI are important in determining mobilization and toxicity. The contents of Cr(VI) and Cr(III) in effluent samples of FI, PI, CI and TFI varied in the ranges [23.0 – 36.0, 2.00 – 7.00], [19.0 – 20.0, 4.00 – 7.00], [9.00 to 23.0, 26.0 – 72.0] and [16.0 – 48.0, 24.0 – 132 mg/L] respectively. The cluster analysis was employed on industrial effluent samples to distribute Cr contamination. A cluster graph is used to detect spatial resemblance in different groups of industrial effluents (spatial variability). The obtained dendrogram categorized all the four sampling industrial effluents into three major clusters, as effluents of PI and FI have lower mutual dissimilarities than industrial effluents of CI and TFI (Figure 1). The comparatively high contents of Cr(VI) were found in effluent samples of FI and PI, because of the large application of dichromate/chromate in these industries . The contents of Cr(VI) in effluent samples of four industries were found to be higher than the U.S. EPA regulatory limit for Cr(VI) (0.05 mg/L). The high levels of Cr(VI) may cause disorders of the skin, gastrointestinal tract, kidney, liver, circulatory, and nerve tissues, as well as lung carcinoma among others . The level of Cr(III) was found to be higher in effluent samples of CI and TFI than FI and PI ($p < 0.05$). The concentration of Cr(III) contents in the industrial effluent samples were within the recommended level of Cr(III) (170 mg/L) in industrial discharges of FI and PI were significantly lower than the level of Cr(VI) may be due to the large application of dichromate/chromate.

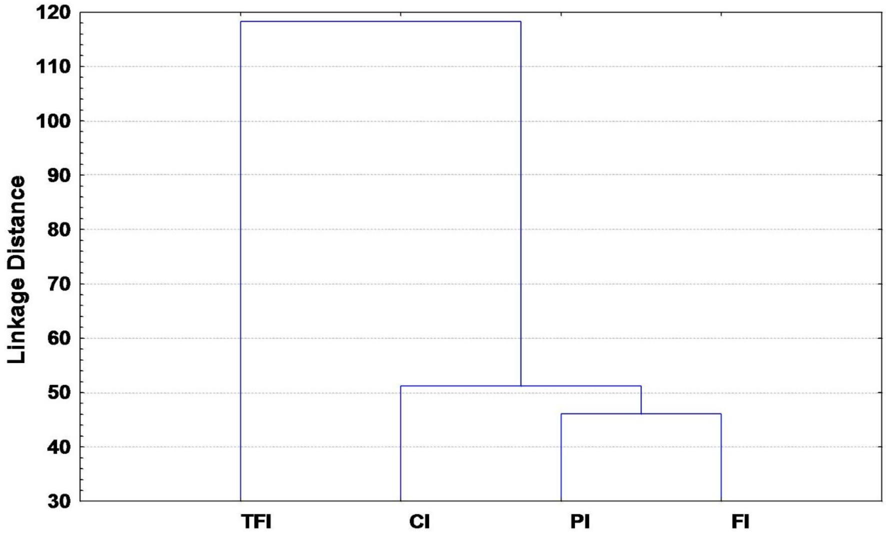

Figure 1: Dendrogram showing clustering of different origins of industrial effluents according to distribution of Cr species.

Table 3: Analytical results of chromium speciation (mg/L) in industrial effluents of different industries of Hyderabad and Jamshoro, Pakistan.

		Total Cr	**Cr(VI)**	**Cr(III)**
FI (n = 30)	Mean ± Std.	34.0±4.00	29.5±6.50	4.50±2.50
	Range	30.0-38.0	23.0-36.0	2.0-7.0
PI (n = 30)	Mean ± Std.	25.0±2.00	19.5±0.50	5.5±1.50
	Range	23.0-27.0	19.0-20.0	4.0-7.0
CI (n = 30)	Mean ± Std.	65.0±30.00	16.0±7.00	49.0±23.00
	Range	35.0-95.0	9.0-23.0	26.0-72.0
TFI (n = 30)	Mean ± Std.	110±70.00	32.0±16.01	78.0±54.00
	Range	40.0-180	16.0-48.0	24.0-132.0

Std. = Standard Deviation

Table 4: Correlation of total Cr with the physicochemical characteristics of industrial effluents.

		pH	**TDS**	**EC**	**BOD**
FI	r –value	0.697	0.874	0.600	-0.821
	p-value	0.00001	< 0.00001	0.0004	< 0.00001
PI	r – value	-0.923	-0.970	0.844	0.881
	p – value	< 0.00001	< 0.00001	< 0.00001	< 0.00001
CI	r – value	0.197	0.124	0.169	0.074
	p – value	0.149	0.514	0.372	0.699
TFI	r – value	0.721	0.653	-0.721	-0.626
	p – value	< 0.00001	< 0.00001	<0.00001	0.0002

The Cr(III) level in the effluent samples of CI and TFI was two to three-fold higher than the Cr(VI) level. It might be due to the large application of Cr(III) salts (nitrate or sulfate) in studied CI and TFI for different industrial processes. The level of Cr(III) in the effluent samples may not have significant toxic effects. Based on the elevated Cr(VI) level in the industrial effluent samples, it is suggested that the effluent of studied industries cannot be used directly for agricultural or other commercial applications. Thus, the level of Cr(III) may be increased due to the conversion of high contents of Cr(VI) discharged from industries into natural water bodies, which may convert into Cr(III) either by the increase in pH up to 7.0 or the dilution by the river or canal water. It is recommended that contaminated industrial effluent could not be discharged into streams of rivers or canals.

The results of total Cr concentration in industrial effluent samples were compared with other previous studies in different countries (Table 5). The total Cr content in industrial effluents samples from district Jamshoro, Pakistan, was found much higher than the reported results in other countries including Pakistan.

The contents of Cr(VI) in industrial effluent samples of the study area were lower than Hyderabad, India and Jeddah, Saudi Arabia and other previous studies from various Scholars . The contents of Cr(III) in industrial effluents of Hyderabad- India, Tabriz-Iran and Jeddah-Saudi Arabia were two to four-fold higher than the contents of Cr(III) in industrial effluents of the study areas .

Table 5: Comparison of previously reported research on total Cr and its species (mg/L) in industrial effluents with this study.

Region	Cr(III)	Cr(VI)	Total Cr	References
Bahia, Brazil	2.63±0.07	--	2.80±0.12	(6)
Denizli, Turkey	16.8±9.6	23.3±5.3	40.1±8.0	(3)
Gaborone, Botswana	--	20.7 ± 0.9	30.7 ± 1.2	(31)
Hyderabad, India	95 ± 2	98.0 ± 2.0	--	(7)
Lucknow, India	--	1.64±0.002	45.1±0.03	(35)
Kasur, Pakistan	--	--	2.10±0.08	(34)
Karachi, Pakistan	--	--	15.2-185	(33)
Tabriz, Iran	46.3 ± 0.8	12.3 ± 0.4	--	(36)
Jeddah, Saudi Arabia	99.0 ± 2.0	99.9 ± 4.0	--	(29)
Jeddah, Saudi Arabia	10.0	--	13.1±0.2	(9)
Jeddah, Saudi Arabia	10.4 ± 0.12	2.4 ± 0.11	12.9 ± 0.1	(32)
Hyderabad and Jamshoro, Pakistan	28.5 ±19.5	74.5±58.0	102±78.0	Current study

These industrial sectors may discharge the untreated effluents into natural water resources through open or closed pathways, which is hazardous to local inhabitants and wildlife. Almost all industries in Hyderabad and Jamshoro either disregarded or partly obeyed international industrial discharge rules. However, some enterprises have established the effluents treatment facility, but this is only a show for the pleasure of national and international organizations.

4. CONCLUSION

The contents of EC, TDS, and BOD in effluent samples of four industries were significantly high than the legal threshold levels set by the US Environmental Protection Agency. Total Cr concentration in textile and fabric industry effluent samples was 400–1800 times greater than the maximum concentration allowed by the US Environmental Protection Agency (EPA). The Cr(VI) was the dominant species in the effluent of FI and PI, but the Cr(III) level is relatively high in the effluent samples of CI and TFI ($p < 0.05$). Cr(VI) levels in effluent samples of four studied industries were higher but below regulatory limits set by the US EPA and WHO. The correlation study indicated that total Cr in effluents of different industries showed a different behaviour with quality parameters depending on the nature of effluent chemical residues. Thus, a continuous assessment and monitoring of the industrial activities is recommended for developing a greener Pakistan. Meanwhile, there is a need for university-industry collaboration to develop industrial eco-friendly and cost-effective solutions.

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